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LABORATORY CORROSION TESTS OF MILD STEEL, WITH SPECIAL REFERENCE TO SHIP PLATE

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ABSTRACT

Prompted by the claim that the ship plates of the *Leviathan* have shown evidence in service of outstanding superior corrosion resistance, a series of corrosion tests of mild steels, including some *Leviathan* and other ship plate, was made by the wet-and-dry and the continuous-immersion methods in sea-salt solutions. The steels varied in copper content from a trace to over 0.60 per cent. No differences in corrosion rate were obtained, indicating marked superior corrosion resistance of any of the compositions used. The differences in corrosion behavior observed were those resulting from difference in the test methods employed. The corrosion rate in the wet-and-dry test decreased as the surface film was built up but was always much higher than that for simple immersion. The laboratory test results have not confirmed in any way whatsoever the claims made for the *Leviathan* plate for unusual superior corrosion resistance.

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I. INTRODUCTION

The statement has frequently been made that the steel ship plate used in the construction of the hull of the *Leviathan* has shown in service a marked superiority in its resistance to corrosion by sea water to that shown by other ship plate. Several years ago the results of comparative tests of some of the original steel plates from the *Leviathan* hull and some steel-plate attachments to the hull, added at the time the ship was used for transport duty in the World War, were reported by Waterhouse.¹ A marked difference in the appearance of the original German steel plates and the added plates, which were of English manufacture, noted when after five years'

¹ G. B. Waterhouse, Tests of Steel Plates of the *Leviathan*, Iron Trade Rev., 75, p. 229; 1924.

service the ship was drydocked, was the reason for carrying out these tests. Waterhouse states:

* * * over five years elapsed between drydocking at Liverpool and at South Boston, during which time no attention or care could be given to the hull plates. Nevertheless, it was found that the bottom was in perfectly clean condition, the hull being free from marine growths, pitting, and corrosion. While the ship was at Liverpool five years before, a skeg of English steel plates was riveted to the stern for carrying a part of the rigging for the paravane or other gear, a mine-sweeping device invented, supplied, and installed by the British Government. In contradistinction to the plates of the hull this skeg, or paravane gear, was found to have been very badly attacked by continuous submersion in the sea water without attention for over five years.

On the basis of the tests carried out, Waterhouse was unable to assign a definite reason for the difference in the corrosion behavior of the two types of ship plate. Possible reasons, which he suggested, for the superiority of the German material were "the presence of a comparatively high percentage of copper and a marked banded structure whereby after moderate corrosion low-carbon layers would be exposed to the sea water." The English steel used for comparison, which was severely corroded during the five years' service, was stated to have the appearance of ordinary acid open-hearth steel with no "marked characteristics to distinguish it from ordinary plate except that copper was present in moderate amount." The copper contents of the two steels given by Waterhouse were 0.169 and 0.134 per cent, respectively, for the *Leviathan* plate and the comparison plate of English manufacture.

The importance which has been attached to the reports of the outstanding superior quality of the *Leviathan* ship plate with respect to corrosion resistance is attested by the fact that within the past two years a large American oil-refining company specified that in the construction of a tanker, which was being built in a foreign shipyard, ship plate similar to that used for the hull of the *Leviathan* should be used.

Other cases of alleged superior corrosion resistance of steel when used in contact with sea water have been reported to the Bureau of Standards from time to time. A recent example of this was some copper-bearing steel piling of foreign manufacture submitted by the Bureau of Yards and Docks, United States Navy Department, the claim being made by the company which furnished this material that the results of 15 years' service in tropical waters indicated a useful life of at least 50 years for this material under the conditions used.

The importance of the question whether or not differences in corrosion resistance of the magnitude illustrated by the cases cited above can be demonstrated in the laboratory is obvious without further discussion. In order to obtain information on this point, corrosion tests of these steels, together with a number of comparison steels,

were carried out. The results of these tests form the basis of this report.

It may be well to emphasize that these tests were not planned with the aim of showing whether or not the claims which have been made concerning the superior corrosion resistance of these steels were true. In fact, it is extremely doubtful whether this question could be definitely answered by the results of laboratory tests alone. However, if the results with a series of materials in the laboratory with corrosion tests, based upon the essential features of the service for which the materials are to be used, show no important or significant differences in the behavior of such materials, the conclusion would seem to be justified that, if marked differences in behavior are noted in service, the underlying cause for such differences should be sought for outside of the material itself. In other words, the composition of the materials would not seem to be the controlling factor in the matter.

II. MATERIALS AND METHODS

1. MATERIALS

Through the cooperation of the Merchant Fleet Corporation of the United States Shipping Board, the United States lines, and the Navy Department two pieces of ship plate ($1\frac{1}{8}$ and $\frac{7}{8}$ inch thick, respectively), which had been removed from the hull of the *Leviathan* in 1924, were secured from the Boston Navy Yard. The sample of copper-bearing steel piling ($\frac{3}{8}$ -inch thick) submitted by the Navy Department has already been mentioned. Samples of ship plate ($\frac{5}{16}$ and $\frac{3}{16}$ inch thick) manufactured by the Vitkovice Steel Works (Vitkovice Mines, Steel & Ironworks Corporation, Vitkovice, Czechoslovakia) for the construction of the oil tanker referred to were secured by the kind cooperation of the oil-refining company for whom this ship was being built.

In addition, a number of other steels were used. Since the copper content of the *Leviathan* steel had been suggested by Waterhouse² as possibly having an important bearing on the alleged unusual behavior of this steel in service, the comparison steels were chosen so as to represent a rather wide range in copper content. Most of these were taken from the series of steels used by committee A-5 of the American Society for Testing Materials in the weather-exposure tests of steel sheet.³ These materials, though not in the form of ship plate, were chosen because their corrosion behavior under various conditions of exposure had already been very carefully observed. The compositions of the different steels used are summarized in Table 1.

² See footnote 1, p. 431.

³ Report of Committee A-5 on Corrosion of Iron and Steel, Proc. Am. Soc. Test. Mtls.; 1918-1928, inclusive.

TABLE 1.—Composition of steels used in the corrosion tests

Designation of material	Nature of material	Composition						
		C	Mn	P	S	Si	Cu	Other elements
L ¹ -----	Leviathan hull plate-----	<i>Per cent</i> 0.15	<i>Per cent</i> 0.43	<i>Per cent</i> 0.088	<i>Per cent</i> 0.078	<i>Per cent</i> 0.01	<i>Per cent</i> 0.13	<i>Per cent</i> As 0.04.
V ¹ -----	Ship plate, Vitkovice Steel Works.	.21	.46	.039	.041	.02	.23	As 0.024.
P ¹ -----	Steel piling, Navy Department.	.16	.73	.056	.034	.01	.23	As 0.013.
SS ² -----	Low-copper pure iron-----	.015	.02	.007	.022	Tr.	.03	
H-----	Copper-bearing basic open-hearth steel.	.07	.39	.016	.027	.004	.24	
II-----	Copper-bearing bessemer steel---	.06	.37	.095	.066	.006	.25	
OO-----	Low-copper open-hearth steel---	.11	.38	.010	.026	.005	.03	Ni. Tr.
C-----	Copper-bearing pure iron-----	.015	.028	.006	.036	.003	.195	
ZZ 712-----	Special (noncommercial) copper-bearing steels.	.06	.39	.045	.043	Tr.	.31	
Z 709-----		.05	.40	.042	.042	Tr.	.47	
Z 702-----		.08	.43	.057	.059	Tr.	.63	
Z 7-----		.065	.35	.112	.047		.022	
ZZ 715 ² -----		.08	.40	.061	.053	Tr.	.36	
1,261 ¹ -----	{Commercial copper-bearing iron sheet.	.02	.11	.005	.010	< .01	.53	{Mo 0.08. As 0.015.

¹ Analysis by H. A. Bright, associate chemist, and C. P. Larrabee, assistant chemist, Bureau of Standards.

² Materials SS to ZZ 715, inclusive, were from the series of steels used by committee A-5, A. S. T. M., the designations used above are those of committee A-5, and the compositions given are those reported by this committee.

Rectangular specimens, 2 by 3½ inches and 2½ by 4 inches, were used for the corrosion tests. The thickness of the specimens varied according to the material from which they were taken. In the case of the sheet the specimens were 2 by 3½ inches, and the full thickness of the sheet was used. In the other cases specimens 2½ by 4 inches ⅛ inch thick were machined from the plate, the specimens being taken so as to represent the material at various distances below the surface in the case of the *Leviathan* plate. The surface area of a specimen was slightly more than 14 square inches (90 cm²) and 20 square inches (129 cm²) for each of the two sizes.

In order to avoid any effect of strain upon the corrosion behavior, the specimens were annealed before being corroded. It is recognized that this does not represent commercial practice, but it was considered necessary in these tests in order that it would be possible to tell whether or not any marked differences in corrosion behavior which might be observed could properly be attributed to composition differences.

The specimens, stacked together in order to minimize oxidation during heating, were annealed in an electrically heated furnace in which a small flame of illuminating gas was burned during the annealing. The specimens were maintained for one hour at 750° C. (1,380° F.) and were allowed to cool in the furnace. The surface of the annealed specimens was cleaned by slight pickling in dilute sulphuric acid (approximately 5 per cent by weight).

2. CORROSION TEST METHODS

A solution of sea salt in distilled water, of the same concentration as that which is often reported for "average" sea water (35 g per liter), was used for the corrosion tests. Some comparison tests were also made with a solution of sodium chloride of the same concentration.

Two methods of applying the solution to the specimens were used. In one the specimens, which were suitably spaced in a supporting rack made of glass rod so that they were not in contact with other specimens or with the sides of the container, were kept immersed in the solution. An enameled cast-iron container having a capacity of slightly less than 2 liters was used. Approximately 1.7 liters of the solution was used in each container with 12 or 15 specimens.

During the test the amount of solution was maintained constant by the addition of water to replace that lost by evaporation.

In the second method, the "wet-and-dry" test, the specimens were repeatedly immersed by an automatic device in the solution, the specimens being held in glass racks which were automatically lowered into the solution at regular intervals (15 minutes) and then withdrawn into the air. The apparatus used for this test has been described and illustrated previously.⁴ The weight of each specimen before being corroded was determined and also at the close of the test after the rust coating had been removed and the specimen cleaned, washed, and dried.

III. RESULTS

1. CLEANING OF SPECIMENS

No difficulty, whatsoever, was experienced in cleaning the specimens after being corroded by the continuous-immersion method. The surface could very easily be wiped free from any of the brown flocculent corrosion product which formed. This was not true, however, of the specimens corroded by the wet-and-dry method. In this case a hard, firmly adhering scale was formed which could be removed only with difficulty. Prolonged soaking of the specimens in a warm solution of ammonium citrate (approximately 10 per cent by weight) was necessary. It was often found expedient to allow the specimens to remain in this solution for 24 hours or so. Even after such a treatment vigorous scrubbing with a stiff bristle or wire brush was required in order to clean the surface completely. The rather wide "scatter" of the points in Figures 1 and 2, representing the results for this wet-and-dry corrosion test, is undoubtedly to be

⁴ H. S. Rawdon and E. C. Groesbeck, Effect of the Testing Method on the Determination of Corrosion Resistance, B. S. Tech. Paper No. 367; 1928.

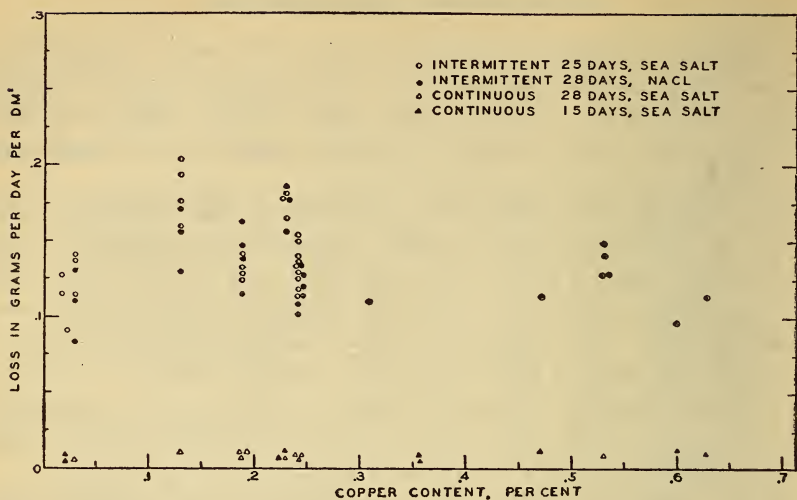


FIG. 1.—Relative corrosion behavior of mild steels of varying copper content when corroded by continuous immersion and by intermittent immersion (wet-and-dry tests)

The solutions contained 35 g of salt per liter. The specimens of *Leviathan* ship plate, 0.13 per cent copper; the specimens of Vitkovice steel plate, 0.23 per cent copper; and the specimens of special steel piling, 0.23 per cent copper, show no marked superiority in their behavior. In most cases, each point plotted represents several samples. For simplicity and clarity, only the average has been given.

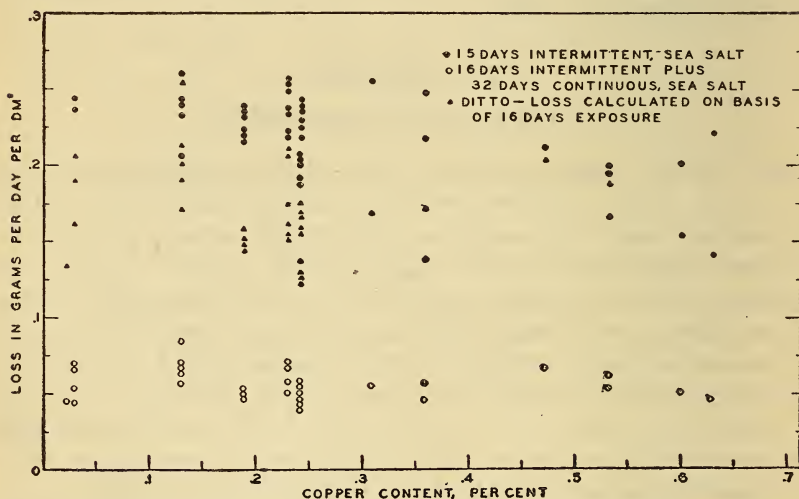


FIG. 2.—Corrosion behavior of mild steels of varying copper content when corroded by the wet-and-dry method in a solution of sea salt, 35 g per liter

Two corrosion rates of the specimens subjected to the combined attack of 16 days' corrosion by the wet-and-dry method and 32 days in simple immersion are given. These have been calculated on the basis of the 48-day period and the 16-day period, respectively.

attributed in part to the method used for obtaining a surface free from any of the corrosion scale.

The behavior of the various steels under corrosion is summarized graphically in Figures 1 and 2. The comparison of the corrosion behavior of the different steels has been made on the basis of the loss of weight occurring during the "runs." The corrosive attack in all cases was decidedly uniform in character, only very slight indications of pitting being noticed in any case. The surface of most of the samples corroded by the repeated immersion method showed a very slight "grooving," the direction of grooving being parallel to the flow of the solution as it drained off the specimen when it was withdrawn from the bath. Evidently this effect is to be attributed to the method of wetting the surface and indicates nothing characteristic of the steel. Nothing of this kind was shown by specimens of the same steel which were corroded by the simple immersion method.

Since all of the materials are essentially the same in density, the loss of weight can be used to represent the comparative behavior of the materials just as well as the depth of penetration or thickness of the metal layer removed.

IV. DISCUSSION

It is very evident from the results in Figure 1 that the method by which the corrosive attack was brought about had a far greater influence upon the apparent corrosion resistance of the various steels used in these tests than the copper content or any other feature in the composition had. All of the steels which were used behaved practically the same when subjected to corrosion by simple immersion as measured by the loss in weight per unit area of surface per day. No difference was observed in the corrosive attack of a sodium chloride solution as compared with the attack produced by a solution of sea salt of the same concentration. The corrosive attack under the conditions of simple immersion used was very slight indeed as compared to that occurring when samples of the same steels were corroded by the wet-and-dry or repeated-immersion method. In neither case did variations in the copper content of the steels, up to 0.60 per cent at least, appear to affect the corrosion resistance of the steels to any marked extent.⁵

The corrosion rate for the steels when corroded by the intermittent immersion method depends upon the length of the test period used. Evidently in the tests of this kind the rate of attack slowly decreases as the test period is prolonged. This is shown by a comparison of the results of the 15-day run (fig. 2) and a 25-day run in a solution of sea salt (fig. 1). These tests were carried out at the same time at

⁵ This is in general agreement with the results of submerged corrosion tests of copper-bearing steel obtained by committee A-5, Corrosion of iron and steel, Am. Soc. Test. Mats., Proc. Am. Soc. Test. Mats., 24 to 28; 1924-1928, inclusive.

room temperature, and the conditions in each were practically identical. It will be noticed, however, that the corrosion rate computed for the 15-day run (fig. 2) was decidedly higher, on the whole, than the rate computed for the 25-day run (fig. 1). This is in accord with the well-known fact that whenever the products of corrosion form an adherent and continuous covering on a metal they constitute a more or less effective barrier against subsequent corrosive attack. Figure 2 also shows the results obtained when a set of specimens, after being subjected to the wet-and-dry test for 16 days, were then immersed continuously in the solution for 32 days. The average corrosion rate for any of these specimens as based upon the 48 days constituting the entire test period was relatively low. The corrosion rate calculated for the period of 16 days, the assumption being made that little or no corrosion occurred after the surface scale had been built up during the initial 16-day period of repeated immersion, was, of course, higher. The corrosion rates based upon the 16-day period, however, are in fair agreement with those of a 15-day run with repeated immersion made independently of the other series.

The scale which formed on the surface of steel when corroded by the wet-and-dry method consisted largely of the magnetic oxide of iron. On the specimens used for these tests the surface coating of the corrosion products, though brown on the outside and also in some cases immediately adjacent to the metal, was for the greater part black in color and was strongly attracted by a magnet when dry. As stated above, the scale adhered very firmly to the steel and could be removed only with difficulty. In the series of tests summarized in Figure 2, in which the specimens were corroded first by the method of repeated immersion for 16 days and then allowed to remain immersed in the solution for 32 days, it was noted that although the scale was still firmly adherent and apparently afforded protection to the underlying steel against further corrosion it could be removed from the specimen much more readily than that from specimens which had been corroded for 16 days by the repeated-immersion method alone. In speculating as to the probable behavior in service of steel which, prior to continuous immersion in sea water, had been corroded in such a manner as to result in the building up of an adherent surface scale it would seem, on the basis of these results, that the coating would in time become less adherent and might eventually flake from the surface.

The examination of samples of corrosion scale which formed on some of the *Leviathan* plates in service and which were removed at the time the ship was dry-docked (1928) showed that the scale formed under service conditions was very similar in appearance to that formed in the laboratory tests. Some of the samples, however, were only slightly magnetic.

The scale which was formed in the wet-and-dry test was essentially the same on all of the steels. Attempts to vary the character of the scale by carrying out the test while the samples were strongly illuminated by the light from a carbon-arc lamp, a set of comparison samples being corroded in the dark, were indecisive. No difference in the visual appearance of the scale formed under these two conditions could be noted. The results of some recent tests in another connection, however, indicate that the solution which is used to wet the surface may have a marked influence on the physical character of the scale. The coating which formed on wrought iron in wet-and-dry corrosion tests carried out with tap water was found to be much more adherent to the metal than the coating formed in similar tests with a solution of sea salt (35 g per liter).

Concerning the practical aspects of the tests, it may be stated that the results of the tests made have not confirmed in any respect the claims which have been advanced concerning the superior corrosion-resistant properties of some of these steels when used as ship plate for marine service. All of the steels used behaved in all essential respects the same when corroded in the same manner. The differences in corrosion rate shown by the tests were due entirely to the different test methods used.

As a result of the inspection of the hull of the *Leviathan* made during the summer of 1928 it was reported to the Bureau of Standards by the Merchant Fleet Corporation of the United States Shipping Board that—

There was very little corrosion evident, and the entire hull was in excellent shape with the exception of small areas around the propellers.

The plates which had been renewed at the Boston Navy Yard approximately seven years ago were inspected, and no difference was noted between the condition of these plates and the condition of the original plates.

It may be concluded, therefore, that the difference in the corrosion resistance reported by Waterhouse for the *Leviathan* plate and the comparison steel does not necessarily indicate superior corrosion resisting properties for the *Leviathan* plate. A satisfactory alternative explanation can be based upon the quite widely different conditions which would be expected to obtain in service for the two materials. Any projecting attachments on the hull of a vessel would be subjected to conditions quite different in many respects from those applying to the hull. In particular, the mechanical or "cavitation" effect of the water would be more severe on both paint and metal, and in all probability the effect of aeration on corrosion would be more pronounced also. Either of these would, in large measure, account for more pronounced attack of the steel attachments as compared with the attack of hull plates.

V. SUMMARY

1. Laboratory corrosion tests in solutions of sea salt and sodium chloride by total immersion ("submerged corrosion") and by repeated immersion ("wet-and-dry corrosion") showed no important differences in the corrosion behavior of a series of steels for either method of attack which could be considered as significant of variations in composition, especially variations in the copper content, which in the series used ranged from practically nil to somewhat more than 0.60 per cent. No pronounced pitting or roughening of the surface occurred as a result of either method of testing other than a very slight grooving which paralleled the lines of flow of the solution in the draining off of the specimen as it was withdrawn from the solution in the wet-and-dry test.

2. The corrosion rate (loss of weight per unit surface area per day) was very uniform for all the steels for submerged corrosion, and this rate of attack was decidedly lower than that for repeated immersion in the same solution for the duration of these tests. During submerged corrosion a brown, flocculent corrosion product which could be very easily removed from the specimens formed.

3. When corroded by the wet-and-dry or repeated-immersion method a firmly adherent hard scale formed over the surface which was removed only with considerable difficulty. As a consequence of the protection afforded by this scale, the corrosion rate decreased as the test period was prolonged. All of the steels used behaved similarly in this respect.

4. The results of the tests carried out do not confirm or substantiate in any way the claims which have been made for the outstanding superior corrosion resistance for some of the steels when used in marine service; for example, ship plate. It is believed that differences in the service conditions, the importance of which has apparently not been fully appreciated, will account satisfactorily for the alleged difference in the corrosion behavior of these steels.

The author very gratefully acknowledges his indebtedness to C. E. Eggenschwiler, junior scientific aid, who by his earnest endeavor has assisted very materially in obtaining the results reported here.

WASHINGTON, November 6, 1928.



